target. Therefore, for future applications, one target will be able to withstand one HPLC run. FIG. 12B (FIG. 3b of the Manuscript) shows that the peaks had a typical short rise time from the base line to the peak (<0.8 s), indicating that the CO_2 pulse band was kept narrow due to the small inner diameter of the capillary used to transport the pulse from the injection system to the ion source. The peak tailing magnitude (x_2-x_0) depended on the amount of injected CO_2 and gas carrier flow. The typical value of the asymmetry factor ($[x_2-x_0]/[x_0-x_1]$) was ~1.8 or ~3.5, measured at 50% or 10% of peak height respectively. The peak tailing was the result of the adsorbed CO_2 and the residual gaseous CO_2 that is not immediately pumped away. The $_{12}C_-$ total charge per pulse, the peak shape and the ionization efficiency were the parameters that we chose to study the performance of the system. Ionization efficiency was defined as the total moles of detected charge (magnet set at m/z=12) relative to the moles of

$$E = \frac{C^-}{C} = \frac{A \times K}{C} \qquad \text{[Equation 2]}$$

carbon from the injected CO_2. See definition in Eq. 2, where A (micro coulombs) is the total charge integrated from the current signal (micro-Amps). K is the inverse of the Faraday constant. C (micro moles)=PV/RT where P, T are the average pressure and temperature of CO_2 in the sample loop registered by both gauges; V is the volume of the sample loop, and R is the gas constant. In short, the simulations offered a first insight in the differences between the conventional diverging-flow and the new directed-flow configurations. Also, the simulated behavior of the CO2 pulses inside the target was reproduced experimentally.

3.3 Adsorption Theory of CO2 on Ti

Our hypothesized mechanism for the CO2 ionization can be described as follow: first CO2 is brought in contact with a Ti surface and is adsorbed; then the high-energy Cs+ particles hit the adsorbed CO2, triggering its fragmentation into C and O elements. The negative charge in the C atoms might be due to electron capture at the Ti surface level. It is known that fragmentation of triatomic molecules can be induced with collisions with energetic particles. The charging of the carbon atoms must occur at surface level because the velocity of the electrons in the gasphase, in a kilovolt potential difference, is too high for being captured by neutral atoms. The adsorption step can be studied using the Jovanovic-Freundlich isotherm models. These two models have been extensively studied individually or in combination in several papers, and the combination is shown in eq. 3, The Freundlich model which is an empiric model for gaseous adsorbates has the form $\theta=(\beta P)v$, where β is a proportional constant.

$$\theta = \frac{q_{ads}}{q_{max}} = 1 - e^{-(\alpha P)^v} \qquad \text{[Equation 3]}$$

In Eq. 3: α is a factor that depends on the CO_2 adsorption rate over the vapor pressure (Eq. 4.), q_{ads} is the specific amount of adsorbed molecules, q_{max} has the same units as q_{ads} and it is the saturation or monolayer capacity of the adsorbent, θ is the fractional coverage or fraction of occupied sites relative to the total availability, P is the partial pressure of the molecule of interest in the bulk near the Ti surface and v is the homogeneity parameter. The amount of adsorbed CO_2 (q_{ads}) is proportional to the measured total charge of $_{12}C_-$ (A), therefore the fractional coverage can be expressed as: $q_{ads}/q_{max}=A/$

A_{max}. P is proportional to the amount of injected CO_2 (C); however it can not be experimentally determined. P can be indirectly measured from the simulation by applying the ideal gas law to the CO_2 transient concentratio. Finally, P is obtained by averaging the transient pressure. As explained earlier, the simulation conditions and constants values were selected by trial and error until matching the amount of injected CO_2 and the experimental peak shape. The Jovanovic model states that every gas particle that reaches the surface is adsorbed only during an average time of residence (r). r can be increased due to collisions with gaseous particles thus the desorbing particle bounces back to the surface.

$$\alpha = \frac{\sigma\tau}{\sqrt{2\pi mkT}} = \frac{e^{(\varepsilon_{ad}-\Delta H_{vap})/RT}}{P_S} \qquad \text{[Equation 4]}$$

In eq. 4: σ is the adsorbate collision cross section (17 Å_2 for CO_2), r is the average residence time; E_{ad} is the adsorption potential energy, ΔH_{vap} and P_s are the heat of vaporization (4.93 KJ/mol) and the vapor pressure (4.92×10$_4$ Torr at 298 K), respectively. mkT are the CO_2 molecule mass, Boltzmann constant and temperature, respectively. These concepts are important for fitting our system because the adsorption process will be controlled by the short transient pressure of the CO_2 pulse in contact with the Ti surface. Examples of the fitting of the Jovanovic-Freundlich model for both configurations. The parameter α will be extracted from the fittings of Eq. 3; E_{ad} and r from Eq. 4. The agreement of the model demonstrates that adsorption must be part of the mechanism of conversion of CO_2 into C−. The fitted parameters of the model are presented in table I. As in any other adsorption system, the data saturate at a point A_{max}. A_{max} is proportional to the total capacity or the total number of available adsorption sites. At a carrier flow of 0.15 mL/min, A_{max} for the directed-flow configuration #1 is 1.8 times bigger than for the diverging-flow configuration even though the area of the Ti surface is the same for both configurations. The reason is that some of the adsorption sites of the diverging-flow configuration are poorly exposed to the CO_2 due to the gas-flow configuration; thus the effective number of adsorption sites is lower. The A_{max} for the directed-flow configuration #1 is 2.2 times larger than for the same configuration with smaller area (#2). In these two configurations, the gas-flow is the same but the areas are simply different, therein the difference in number of adsorption sites. The parameter v measures the homogeneity of the surface. All the Ti surfaces had the same degree of homogeneity (flat and smooth); however the CO_2 gas is differently distributed on the Ti surface for the directed-flow and diverging-flow configurations. Therefore, this difference in distribution translates into different values for the surface homogeneity parameter. Logically, v presents almost the same value for the directed-flow configurations. Eq. 4 states that α, E_{ad} and r are independent of the geometry and only depends on the thermodynamics of the surface-adsorbate interaction, and the experimental results agree with this. Our r values agree with Jovanovic who estimated that r should be 10$_{-6}$ to 10$_{-10}$ s in the case of physical adsorption. Vesselli et al. using Density Functional Theory (DFT), investigated the adsorption energy (E_{ad}) of CO_2 on several metals. Some examples of these values in eV are: 0.09, 0.11 and 0.32 for Cu, Pt and Ni, respectively. Cu seems to have low affinity for CO2 while Ni has high affinity. In this work, we determined an Ead of 0.26 eV for Ti which means high affinity but lower than Ni. As stated in the introduction, it was expected that Ti will have higher affinity than Ni; however the experimental conditions